Grain size limit for SD hematite

Günther Kletetschka [a,*], Peter J. Wasilewski [b]

[a] *Code 691, GSFC/NASA, Greenbelt, MD 20771, USA*
[b] *Code 921, GSFC/NASA, Greenbelt, MD 20771, USA*

Abstract

Grain sizes in the range (10^{-4} to 10^{-1} mm) are common in some rocks. Because thermal and/or chemical remanent magnetization of hematite in this range approaches intensities of single domain (SD) magnetite, careful exploration of this transition, may serve to develop new applications in rock magnetism that relate to magnetic anomaly source identification, and various paleomagnetic and grain size-dependent investigations.

Grain size-dependent magnetic behavior of hematite reveals a SD–multidomain (MD) transition at 0.1 mm. This transition is recognized by variation in magnetic coercivity and susceptibility and is related to an anomaly in remanence recovery when cycling through the Morin transition. The coercivity decrease with increasing grain size occurs much more gradually above 0.1 mm than below this value. Magnetic susceptibility of the grains smaller than 0.1 mm has negligible dependence on the amplitude of the applied alternating magnetic field. For the larger grains a new amplitude-dependent susceptibility component is observed. The grain size of 0.1 mm is also associated with loss of most of the remanence when cycling through the Morin transition. This behavior is ascribed to a transition from the metastable SD to the MD magnetic state. The increase in magnetized volume causes the demagnetizing energy to destabilize the SD state, resulting in a transition where the demagnetizing energy is reduced by nucleation of the domain wall for grains larger than 0.1 mm. The 0.1 mm transition has no significant effect on shape of the temperature-dependent coercivity and saturation magnetization. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hematite; Grain size; Domains; Magnetic properties; Morin transition; Susceptibility; Hysteresis

1. Introduction

Recent work on pure natural hematite (Kletetschka et al., 2000a) examined acquisition of thermoremanent magnetization (TRM) in weak external magnetic fields. TRM is acquired when a magnetic mineral (e.g. hematite) is demagnetized by heating above its Curie temperature and subsequently cooled down in the presence of a weak magnetic field (usually geomagnetic). The intensity of TRM of hematite (acquired at 0.05 mT) systematically increases across a fairly large interval of grain sizes (10^{-4} to 10^{-1} mm). This increase appears to plateau at the 10^{-1} mm grain size beyond which the TRM intensity stays more or less constant (Fig. 1 in Kletetschka et al., 2000a). The grain sizes in the range 10^{-4} to 10^{-1} mm are common in natural settings and thus careful exploration of this transition region, characterized by the onset of large intensities of TRM, may serve to stimulate new applications in rock magnetism that utilize grain size-dependent properties.

Hematite contains both a spin canted (Dzyaloshinsky, 1958) and a defect moment (Gallon, 1968). The defect moment is generally attributed to foreign cations, but it also can occur from other defects, such as the ordering of vacancies in the basal plane. Both moments can contribute to the magnetization above

* Corresponding author. Tel.: +1-301-286-3804;
fax: +1-301-286-0212.
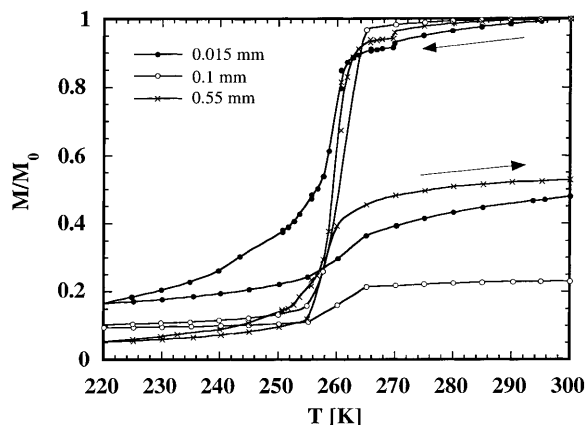*E-mail address:* gunther.kletetschka@gsfc.nasa.gov
(G. Kletetschka).

Fig. 1. Morin transition cycling for various grain sizes of hematite. Samples were initially saturated in 5 T external magnetic field at room temperature, and then cooled to 220 K and warmed to 300 K in zero field.

the Morin transition, but the spin canted moment vanishes below the Morin transition.

Many magnetic aspects of different grain size of hematite are contrary to conventional wisdom. When grain size increases a homogeneously magnetized volume (single domain (SD)) divides into multiple homogeneously magnetized sub-volumes (multidomain (MD)) separated by domain walls. The coercive force is conventionally a measure of the grain size dependence of these magnetic states. As expected, the coercive force of MD hematite is much less than that of SD hematite (Kletetschka et al., 2000a,b). Despite this behavior the TRM intensity is most intense for grain sizes of hematite generally considered to be in MD states (this grain size-dependent remanent characteristic seems to be valid for chemical remanent magnetization (CRM) as well, according to Clark (1997)). MD-sized hematite grains acquire TRM that is more than 50% of the room temperature saturation remanent isothermal magnetization (SIRM) when cooling through the Curie point in the geomagnetic field (Kletetschka et al., 2000b). This property implies a uniquely large REM value (TRM/SIRM ratio) commonly not observed in natural materials. Of all the natural magnetic minerals studied thus far only the coarse-grained hematite samples have a REM value much greater than 0.1. This important magnetic property of hematite has been overlooked

in the past and can serve as a significant identification parameter for coarse-grained hematite. The only large REM values observed before were considered to be associated with contamination and/or with lightning strikes (Wasilewski and Kletetschka, 1999; Wasilewski, 1977). Apart from hematite and titanohematite all common magnetic minerals have TRM values much more than order of magnitude less than their SIRM values and this property has been used in various applications (Wasilewski, 1977; Kletetschka et al., 2000b; Clark, 1997; Cisowski and Fuller, 1986; Cisowski et al., 1990; Fuller et al., 1988). Hematite exhibits an inverse TRM grain size dependence across the SD transition compared to all other minerals found in the crust (Kletetschka et al., 2000a). This is likely to be due to a weaker influence of the demagnetizing energy (relates to a maximum magnetic response to the increasing external magnetic field) with respect to wall pinning energy (defined by nature of lattice impurities within the mineral) in the case of hematite, at temperatures almost up to the Curie temperature (Kletetschka et al., 2000a). Another contributing factor is the greater importance of the magnetostatic energy in an applied field, which for hematite dominates the total energy at high temperatures. Thermal blocking only occurs just below the Curie temperature in MD hematite, because of the large volume associated with Barkhausen moments in such grains (Kletetschka et al., 2000a).

2. Material and method

Pure natural hematite sample L2, from Central Labrador (Kletetschka, 1998), characterized by X-ray diffraction and Curie temperature measurements (Kletetschka et al., 2000a), was crushed and sifted to obtain average grain sizes of 1, 0.55, 0.2, 0.1, 0.05, 0.038, 0.025, and 0.015 mm using USA standard testing sieves.

The individual grain size fractions (∼200 mg) were placed in the gelatin capsules for Morin transition measurements. Morin transition is a magnetocrystalline transition that occurs near 255 K. Above the Morin transition the spins are in the basal plane of hematite while below the transition they are along the ternary axis. Using the cryogenic susceptometer MPMS2 (Quantum Design) Morin transition tem-

124 peratures were measured at the Institute for Rock
125 Magnetism (IRM), University of Minnesota. The
126 variation of SIRM acquired at room temperature was
127 measured during a decrease of the temperature down
128 to 220 K and subsequent cycling back to room tem-
129 perature (300 K). This thermal variation allows to
130 monitor magnetic changes across the Morin transition
131 (255–260 K). After this experiment samples inside
132 MPMS2 were exposed to different magnitudes of
133 alternating magnetic field whose frequency varied be-
134 tween 0.03 and 30 Hz. The magnetic response of the
135 samples was expressed in terms of magnetic suscep-
136 tibility. Temperature-dependent hysteresis loops were
137 also done at IRM. VSM was equipped with electri-
138 cal oven capable of heating the grain size fraction
139 up to 700°C in air and atmospheric pressure. Finally
140 the hysteresis properties of all sample fractions were
141 measured at room temperature on a vibrating sample
142 magnetometer (VSM) at the Goddard Space Flight
143 Center facility using magnetic fields up to 2 T.

144 ## 3. Results

145 The characteristic low temperature curves for three
146 representative grain sizes (0.55, 0.1, and 0.015 mm)
147 show sharp Morin transitions (Fig. 1), however, the
148 detailed character of the transition seems to depend
149 on the grain size. This is likely a result of sample
150 preparation (grinding induced ordered defects).

151 The moment seen in Fig. 1 below the Morin transi-
152 tion must be a defect moment. Notice that this moment
153 appears to increase with a decrease in mean grain size.

154 The fraction of magnetic remanence recovered after
155 low temperature cycling is shown in Fig. 2. The recov-
156 ered remanence seems to be extremely sensitive to the
157 grain size used in this experiment. This may have to do
158 with increasing difficulty of domain wall nucleation as
159 the grain size decreases (Boyd et al., 1984). The mini-
160 mum value of recovered remanence was found for the
161 grain size in between 0.1 and 0.05 mm. This grain size
162 range correlates with the magnetic remanence acquisi-
163 tion transition observed by Kletetschka et al. (2000a).

164 Hysteresis loops for various grain sizes (Fig. 3)
165 show major change in the coercivity trend (Fig. 2).
166 For grain size less than 0.05 mm the coercivity rapidly
167 decreases at a rate of 80 mT per two-fold increase in
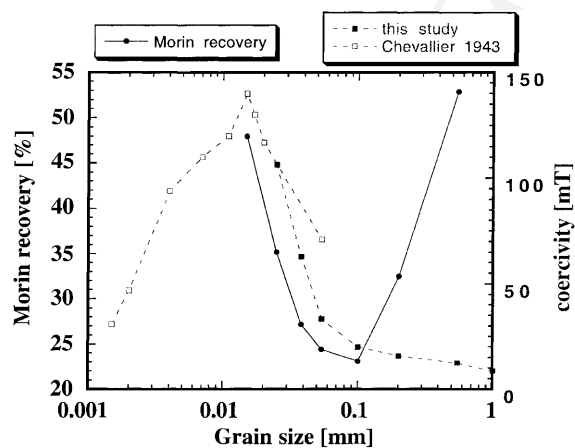168 grain size. For grain size greater than 0.05 mm, the co-

Fig. 2. Plots of room temperature coercive force (squares) vs. grain size, and the magnetic memory recovery (solid dots) after cycling through the Morin transition identify the magnetic change near the 0.1 mm grain size. Coercivity data for smaller grain sizes are taken from Chevallier and Mathieu (1943).

169 ercivity rate of decrease rapidly changes and stabilizes
170 for grain sizes larger than 0.1 mm. The coercivity rate
171 of decrease for grain size above 0.1 mm is much less
172 and amounts to 2 mT of coercivity drop per two-fold
173 increase in grain size (Fig. 2).

174 The ratio between saturation remanent magnetiza-
175 tion and saturation magnetization (M_{rs}/M_s) decreases
176 monotonously with grain size and does not show any
177 major change for this grain size range (Fig. 4).

178 The change in the magnetic susceptibility of
179 hematite with the amplitude of the external alternat-
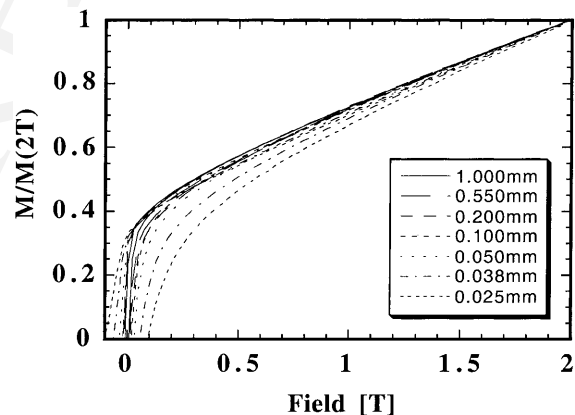

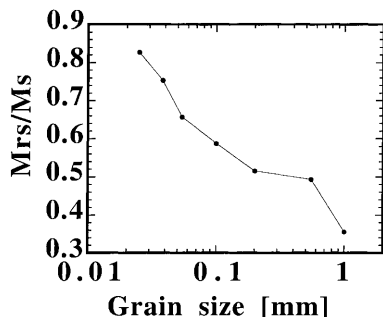Fig. 3. Hysteresis loops for various grain sizes of hematite.

Fig. 4. Squareness ratio (Mrs/Ms) for various grain sizes of hematite.

ing magnetic field (3 Hz) for various grain sizes are shown in Fig. 5. Susceptibility decreases uniformly with grain size for all amplitudes of alternating magnetic field when grains are smaller than 0.1 mm. Susceptibility for grains larger than 0.1 mm change with increase of alternating field amplitude dependence and lacks grain size sensitivity for smaller amplitudes of alternating magnetic field. The susceptibility was observed to slightly decrease (<2%) when frequency changed from 0.03 to 30 Hz with no apparent grain size dependence.

Hysteresis loops were run for grain size fractions: 0.2, 0.1, and 0.05 mm at various temperatures up to the Curie point of hematite. Temperature-dependent hysteresis parameters (saturation magnetization $= J_s$ and coercivity H_c) were calculated and the resulting curves were normalized (see Fig. 6).
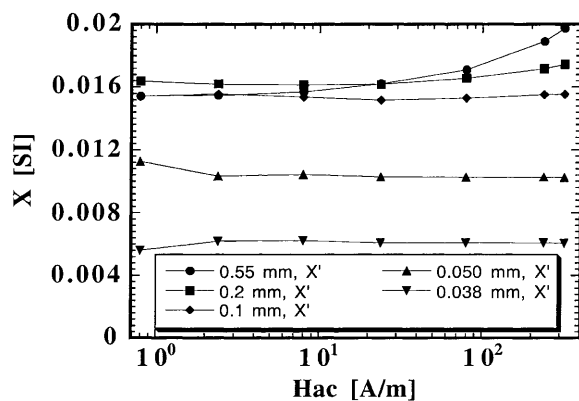

Fig. 5. Susceptibility variation, as a function of the amplitude of the alternating magnetic field H_{ac} (3 Hz), for indicated grain sizes of sized hematite L2.
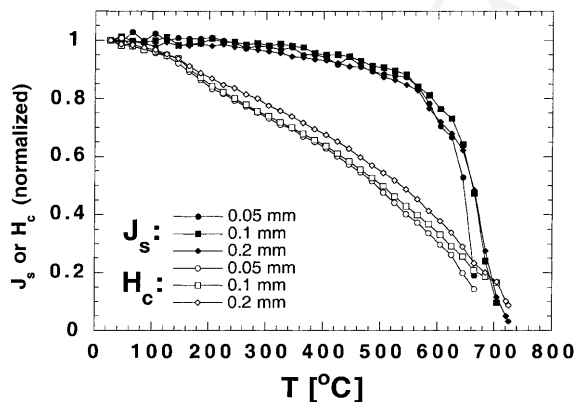

Fig. 6. Saturation magnetization (J_s) and coercivity (H_c) variations with temperature for indicated grain sizes of sized hematite L2.

4. Discussion

Néel's theory for SD grains predicts an increase of remanent magnetization as grain size increases (Néel, 1955) due to more efficient alignment of individual magnetic moments. This is consistent with the increase of TRM within the grain size 10^{-4} to 10^{-1} mm (Kletetschka et al., 2000a, equation 3, Fig. 1). However, Fig. 2 shows a coercivity decrease for grain sizes smaller than 0.015 mm (see also Chevallier and Mathieu, 1943). Banerjee (1971) interpreted this decrease as due to an increasing admixture of superparamagnetic grains in the crushed samples.

The observed minimum in the remanence recovery after cooling through the Morin transition (Fig. 2) suggests that grain size 0.1 mm corresponds to the volume at which the increase in magnetostatic energy renders the SD state unstable. This is indicated by the minimum of the remanence recovery when cooling through the Morin transition.

The maximum in coercive force at ∼0.015 mm in Fig. 2 is thought to define the critical SD size (Banerjee, 1971), i.e. the size above which the global energy minimum state contains at least one domain wall. Grains approximately 0.1 mm in size probably represent the upper limits for metastable SD behavior. Between these two sizes a significant proportion of the hematite grains fail to nucleate domain walls after exposure to a saturating field and remain in a quasi-saturated local energy minimum state. After cooling below the Morin transition, the grains

can nucleate a domain wall, in response to the de-magnetizing field of the grain, during rewarming in zero field. This metastable SD — two domain transition occurs more readily with increasing grain size within the 0.015–0.1 mm range, as the demagnetizing energy becomes more important for larger grains. Observations of domain patterns and hysteresis loops of individual hematite grains have shown the existence of quasi-saturated metastable SD states and the importance of wall nucleation in controlling hysteresis (Halgedahl, 1995; Boyd et al., 1984). Grains substantially larger than 0.1 mm, however, contain several domain walls. The mechanism of low temperature memory in such grains is not well understood (Dunlop and Özdemir, 1997, p. 72). However, domain observations during cycling through the Morin transition indicate that walls in large grains, which disappear below the transition, tend to reform in similar positions to the pre-cooling configuration after rewarming (Gustard, 1967; Gallon, 1968; Eaton and Morrish, 1969). In these MD grains the wall positions may be constrained by pinning sites, which displace them from their equilibrium positions and produce a remanence that is restored after the domain pattern is re-established following low temperature cycling. Thus, true MD hematite grains exhibit substantial low temperature memory, whereas metastable SD grains that nucleate a wall after cycling through the Morin transition undergo the most drastic loss of remanence.

Amplitude dependence of susceptibility has been observed for titanomagnetite (Jackson et al., 1998) and pyrrhotite (Worm, 1991; Worm et al., 1993). It is absent in pure magnetite (Jackson et al., 1998). Hematite has distinct susceptibility behavior for grain sizes smaller and larger than 0.1 mm. Approaching 0.1 mm from smaller grain sizes (<0.1 mm) is characterized by an increase in susceptibility with negligible dependence on the alternating amplitude of the magnetic field. However, as soon as the grain size increases above 0.1 mm an increase in susceptibility is observed at higher amplitudes of alternating magnetic field (Fig. 5). Because the effects of self-demagnetization on the observed susceptibility are negligible for hematite (0.02 SI) the field dependence of the intrinsic susceptibility is readily observable. Magnetite grains by contrast have much higher intrinsic susceptibilities (>10 SI) and any grain size dependence of susceptibilities is suppressed by self-demagnetization.

Susceptibility results indicate that the coercivity of hematite grains lowers as the grain size approaches 0.1 mm. This behavior is prescribed to the increase of metastability of the hematite SD magnetic state. Grains are still in SD magnetic state and have their entire volume magnetized in one direction within the basal plane. The increase in magnetizing volume causes the demagnetizing energy to reach balance with the magnetic stability of SD. This energy balance results in transition between the SD magnetic state and the new magnetic state where the demagnetizing energy is satisfied by nucleation of the domain wall causing an initiation of MD character of grains larger than 0.1 mm. But just before this grain size threshold is reached, the magnetic grains respond to the alternating magnetic field by rotation of the entire volume of magnetization and thus the susceptibility is determined by the viscosity of the magnetic moment to rotate within the basal plane. According to Fig. 5, magnetic susceptibility of this process seems to be independent of the magnetic field amplitude. With onset of the domain wall nucleation for grain sizes >0.1 mm the magnetic response to the applied field increases with field amplitude. This is because the mechanism of the response of the domain wall to the demagnetizing field relates to the magnetic interaction of the domain wall inside the hematite grain and not to the rotation of the entire magnetic moment within the plane perpendicular to the c-axes. Thus, low amplitudes affect the entire volume like in the SD case for small grain sizes. However, with the introduction of the large amplitudes of magnetic field the domain walls add additional susceptibility component that increases with the grain size due to increase of the domain wall population.

The susceptibility of metastable SD hematite grains, like that of stable SD particles, arises from rotation of the whole grain moment against the basal plane anisotropy. For applied fields less than the anisotropy field, this susceptibility is independent of applied field intensity. For grains containing domain walls, however, the susceptibility reflects an additional component due to wall displacement. If the shape of the energy wells associated with wall pinning sites are not parabolic, or if the domain structure itself is modified by the applied field, this component of

susceptibility is field-dependent. Thus, the field dependence of susceptibility, plotted for each grain size in Fig. 5, suggests that grains less than or equal to 0.1 mm are metastable SD, whereas the larger grain sizes, with field-dependent susceptibility, are MD. Finally, it should be noted that critical sizes for the SD — metastable SD and metastable SD — MD transitions are likely to differ for different hematite grains, even when the compositions are identical. Because the basal plane anisotropy is predominantly of magnetoelastic origin (Eaton and Morrish, 1969; Dunlop and Özdemir, 1997, p. 72), domain wall energies and widths vary widely, depending on the internal stress distribution in each grain. Thus, even for assemblages with narrow grain size distributions, magnetic properties of individual grains will exhibit broad distributions and magnetic properties of assemblages should show gradual, rather than sharp, dependence of magnetic properties on average grain size, as is found for the hematite grains studied here. This relation is illustrated in Fig. 6 where the thermal dependence of coercivity and saturation magnetization across the 0.1 mm transition does not change much. However, the grain size dependence of data in Fig. 6 allow direct determination of proportionality factor n (see equation 4 in Kletetschka et al., 2000b) and allows a calculation of theoretical TRM acquisition curves for different grain sizes fitting experimental TRM acquisition curves (Dunlop and Kletetschka, 2001).

5. Conclusion

Coercivity and Morin transition data support the existence of significant magnetic transition at the 0.1 mm grain size of hematite. Below this transition hematite grains have SD like behavior. The onset of true MD behavior with increasing grain size can be monitored through the change of magnetic coercivity and through observation of the minimum in the remanence recovery when cycling through the Morin transition. Another magnetic signature of this transition is revealed by measuring magnetic susceptibility as function of grain size. Magnetic susceptibility of SD grains has negligible dependence on amplitude of the applied alternating magnetic field. With introduction of the domain walls, for grains above 0.1 mm another magnetic field amplitude-dependent susceptibility component is introduced allowing a clear distinction between the domain state of different grain sizes. $J_s(T)$ and $H_c(T)$ curves do not change dramatically across this transition.

Acknowledgements

References

Banerjee, S.K., 1971. New grain size limits for paleomagnetic stability in hematite. Nature Phys. Sci. 232, 15–16.

Boyd, J.R., Fuller, M., Halgedahl, S., 1984. Domain wall nucleation as a controlling factor in the behavior of fine magnetic particles in rocks. Geophys. Res. Lett. 11, 193–196.

Chevallier, R., Mathieu, S., 1943. Proprietes magnetiques des poudres d'hematite-influence des dimensions des grains. Annales Phys. 18, 258–288.

Cisowski, S.M., Fuller, M., 1986. Lunar paleointensities via the IRMs normalization method and the early magnetic history of the moon. In: Hartmann, W.K., Phillips, R.J., Taylor, G.J. (Eds.), Origin of the Moon. Lunar and Planetary Institute, Houston, pp. 411–424.

Cisowski, S., Dunn, J., Fuller, M., Wasilewski, P.J., 1990. NRM: IRM(s) demagnetization plots of intrusive rocks and the origin of the their NRM. Tectonophysics 184, 35–54.

Clark, D.A., 1997. Magnetic petrophysics and magnetic petrology: aids to geological interpretation of magnetic surveys. J. Aust. Geol. Geophys. 17, 83–103.

Dunlop, D.J., Özdemir, Ö., 1997. Rock Magnetism: Fundamentals and Frontiers. Cambridge University Press, Cambridge, 573 pp.

Dunlop, D.J., Kletetschka, G., 2001. Why does multidomain hematite acquire intense TRM? GRL, in press.

Dzyaloshinsky, I., 1958. A thermodynamic theory of "weak" ferromagnetism of antiferromagnetics. J. Phys. Chem. Solids 4, 241–255.

Eaton, J.A., Morrish, A.H., 1969. Magnetic domains in hematite at and above the Morin transition. J. Appl. Phys. 40, 3180–3185.

Fuller, M., Cisowski, S., Hart, M., Haston, R., Schmidtke, E., 1988. NRM:IRM(s) demagnetization plots: an aid to the interpretation of natural remanent magnetization. Geophys. Res. Lett. 15, 518–521.

Gallon, T.E., 1968. The ferromagnetic domain structure of hematite. Proc. Royal Soc. London 303, 525–529.

Gustard, B., 1967. The ferromagnetic domain structure of hematite. Proc. Royal Soc. London 297, 269–274.

Halgedahl, S.L., 1995. Bitter patterns versus hysteresis behavior in small single particles of hematite. J. Geophys. Res. 100, 353–364.

Jackson, M., Moskowitz, B., Rosenbaum, J., Kissel, C., 1998. Field-dependence of ac susceptibility in titanomagnetites. Earth Planetary Sci. Lett. 157, 129–139.

Kletetschka, G., 1998. Petrogenetic grids and their application to magnetic anomalies in lower crustal rocks, Labrador. Department of Geology and Geophysics, University of Minnesota, 157 pp.

Kletetschka, G., Wasilewski, P.J., Taylor, P.T., 2000a. Unique thermoremanent magnetization of multidomain sized hematite: implications for magnetic anomalies. Earth Planetary Sci. Lett. 176, 469–479.

Kletetschka, G., Wasilewski, P.J., Taylor, P.T., 2000b. Hematite versus magnetite as the signature for planetary magnetic anomalies. Phys. Earth Planetary Interiors 119, 259–267.

Néel, L., 1955. Some theoretical aspects of rock magnetism. Adv. Phys. 4, 191–243.

Wasilewski, P.J., 1977. Magnetic and microstructural properties of some lodestones. Phys. Earth Planetary Interiors 15, 349–362.

Wasilewski, P., Kletetschka, G., 1999. Lodestone: natures only permanent magnet, what it is and how it gets charged. Geophys. Res. Lett. 26, 2275–2278.

Worm, H.U., 1991. Multidomain susceptibility and anomalously strong low field dependence of induced magnetization in pyrrhotite. Phys. Earth Planetary Interiors 69, 112–118.

Worm, H.U., Clark, D., Dekkers, M.J., 1993. Magnetic susceptibility of pyrrhotite: grain size, field and frequency dependence. Geophys. J. Int. 114, 127–137.